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# **Determination of $^{99}\text{Tc}$ in Environmental Samples by Anion Exchange**

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**Abstract.** The chemical yield of technetium by an anion exchange (AG 1-X<sub>4</sub>) procedure is determined under different conditions from 200 liters sea water. A new method for collecting  $^{99}\text{Tc}$  from 200-400 liters sea water has been developed by anion exchange. The evaporation rates of  $\text{RuO}_4$  and  $\text{TcO}_4^-$  are determined at 100°C in 0.1 N  $\text{H}_2\text{SO}_4$ . A higher decontamination factor  $2.5 \times 10^5 - 2.4 \times 10^7$  for ruthenium is obtained by evaporating the  $\text{RuO}_4$  at 100°C in 0.1 N  $\text{H}_2\text{SO}_4$ . The ruthenium is oxidized to  $\text{RuO}_4^-$  with  $\text{NaClO}$  at  $\text{pH} = 9$ .  $\text{Fe}(\text{OH})_3$  scavenging,  $\text{AgCl}$  precipitation and 5% TIOA/xylene extraction at controlled valence are used for decontamination of ruthenium,  $^{110\text{m}}\text{Ag}$  and other nuclides. The chemical yield of technetium-99 in the procedure is about 70%.

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# Introduction

Previous work<sup>1</sup> has demonstrated that an anion exchange separation step may be used for the purification of a technetium-99 sample. We have developed a purification procedure<sup>2</sup> which is a solvent extraction at controlled valence. The technetium-99 is taken from large volume sea water samples collected by  $\text{Fe}(\text{OH})_2$  precipitate. A large amount of iron is included in the technetium sample. This makes it difficult to purify the sample.

It was therefore necessary to develop a new method for collecting the technetium-99 from large volumes of sea water and for ruthenium decontamination from the technetium sample.

## Experimental

1. Determination of the chemical yield of technetium-99 for anion exchange from 200 litres sea water by 3 different pretreatments:

- a) Filter the 200 litres sea water through a filter paper in order to separate the algae etc. Add  $^{99\text{m}}\text{Tc}$  tracer and 100 ml 30%  $\text{H}_2\text{O}_2$  to the sea water. Stir with air for 30 min to get  $\text{TcO}_4^-$  and to allow isotope exchange to be completed. Acidify the 200 litres sea water to  $\text{pH} = 1$  with concentrated  $\text{H}_2\text{SO}_4$ . Stir 30 min again. Prepare three  $11 \times 2.5$  cm (i.d.) anion exchange (AG1-X<sub>4</sub> 100-200 mesh) columns. Load the resin by passing the 200 litres sea water through the 3 columns with a pump (see Figure 1). The speed is 50 ml/min for each column. Wash with 500 ml distilled water, 500 ml 0.1 N  $\text{HNO}_3$  and 100 ml 1 N  $\text{HNO}_3$  for each column. Strip with 200 ml 10 N  $\text{HNO}_3$  for each column. After 25 ml, wait 80 min for ion exchange. It takes 2 hours to finish the stripping. Measure the chemical yield.
- b) Filter the 200 l sea water. Add  $^{99\text{m}}\text{Tc}$  tracer. Stir with air pump for 1 h to get a uniform mixture. Give same treatment as described under a).
- c) Filter the 200 litres.  $^{99\text{m}}\text{Tc}$  is reduced to  $^{99\text{m}}\text{Tc}^{+4}$  by adding a solution containing 2 mg/ml  $\text{K}_2\text{S}_2\text{O}_5$  in 0.5 N  $\text{HCl}$  for 1 h. Add the  $^{99\text{m}}\text{Tc}^{+4}$  to the 200 litres sea water. Stir with air for 1 h to get a uniform mixture. Continue as described under a).

The results are shown in Table 1 (see Appendix 1).

2. Determination of  $^{103}\text{Ru}$  evaporation rate in the 0.1 N  $\text{H}_2\text{SO}_4$  solution:

Add  $^{103}\text{Ru}$  tracer, 0.5 ml 5 mg  $\text{RuCl}_3/\text{ml}$  carrier and 2 ml 5%  $\text{NaClO}$  to 100 ml beaker. Add  $\text{NaOH}$  to the solution to get  $\text{pH} = 9$ . Heat 10 min to get  $\text{RuO}_4^-$  and to allow isotope exchange to be completed. Acidify the solution to  $\text{pH} = 1$  with  $\text{H}_2\text{SO}_4$ . Heat the solution to evaporate the  $\text{RuO}_4$ . Measure the counts of  $^{103}\text{Ru}$  at different times comparing with a standard source. The evaporation rate of the  $\text{RuO}_4$  is shown in Table 2 (see Appendix 1).

3. Determination of technetium evaporation rate in 0.1 N  $\text{H}_2\text{SO}_4$  at  $100^\circ\text{C}$ .

Add  $^{99\text{m}}\text{Tc}$ , ruthenium carrier 5 mg  $\text{RuCl}_3/\text{ml}$  and 2 ml 5%  $\text{NaClO}$  to a 100 ml beaker. Adjust  $\text{pH} = 9$  with  $\text{NaOH}$ . Heat for 10 min to get a uniform mixture. Acidify the solution to  $\text{pH} = 1$  with  $\text{H}_2\text{SO}_4$ . Heat for 30 min in order to evaporate the  $\text{RuO}_4$  (carrier). Repeat the operation two times more.

Measure the chemical yield of  $^{99m}\text{Tc}$  (cf. Table 3 in Appendix 1).

## Procedure

### Principle

The  $\text{TcO}_4^-$  is intensely absorbed on an anion exchange resin<sup>3</sup>. It is therefore difficult to strip the  $\text{TcO}_4^-$ , but it may be done by a higher affinity group  $\text{NO}_3^-$ . The high chemical yield of  $^{99m}\text{Tc}$  for anion exchange is shown in Table 1. This is the first step for separating the technetium from lower valence cation and a large amount of salt. The second step is oxidation of the technetium and ruthenium to  $\text{RuO}_4^-$  and  $\text{TcO}_4^-$  with 5%  $\text{NaClO}$  at  $\text{pH} = 9$ . Acidify the solution to  $\text{pH} = 1$  with  $\text{H}_2\text{SO}_4$ . Heat the solution at  $100^\circ\text{C}$ . The  $\text{RuO}_4$  is evaporated. But the  $\text{TcO}_4^-$  is left in the solution as shown in Tables 2 and 3. This step is taken especially to decontaminate the ruthenium.

The  $\text{Fe}(\text{OH})_3$  scavenging and  $\text{AgCl}$  precipitate are used for cleaning for  $^{110m}\text{Ag}$  and other nuclides. This is the third step.

The fourth step is decontaminating for ruthenium and other nuclides by extraction of the  $\text{TcO}_4^-$  leaving the ruthenium in 1 N  $\text{H}_2\text{SO}_4$ . The valence is controlled with  $\text{H}_2\text{O}_2$  by 5% TIOA/xylene extraction.

Determination of chemical yield of  $^{99}\text{Tc}$  and decontamination factor for  $^{103}\text{Ru}$  of the procedure.

1. Acidify 10 litres sea water to  $\text{pH} = 1$  with  $\text{HCl}$ . Add 32 g  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ,  $^{99m}\text{Tc}$ , 60 g  $\text{K}_2\text{S}_2\text{O}_5$ . Shake to get a uniform mixture. Let stand for 1 h to get  $\text{Tc}^{+4}$ .
2. Add  $\text{NH}_4\text{OH}$  to  $\text{pH} = 9$ . Let stand for 4 h. Discard the sea water. Centrifuge. Dissolve the  $\text{Fe}(\text{OH})_3$  with 60 ml 10 N  $\text{H}_2\text{SO}_4$ . Add 60 ml 15%  $\text{NaClO}$  to get  $\text{TcO}_4^-$ . Add 0.5 ml (5 mg/ml)  $\text{AgNO}_3$ . Heat for 30 min. Cool and filter the solution. Dilute to 600 ml to get 1 N  $\text{H}_2\text{SO}_4$ .
3. Add solution to column 11 cm  $\times$  0.7 cm (AG1-X<sub>4</sub> 50-100 mesh). The speed is about 10 ml/min.
4. Wash with 100 ml ion exchange water, 100 ml 0.1 N  $\text{HNO}_3$  and 40 ml 1 N  $\text{HNO}_3$ .
5. Strip with 50 ml 7 N  $\text{HNO}_3$ . After 5 ml, wait for 30 min for ion exchange. It takes 50 min to finish the stripping.
6. Evaporate solution to 0.2 ml.
7. Add  $\text{NaOH}$  to  $\text{pH} = 9$ , 2 ml 5%  $\text{NaClO}$ , 0.4 ml  $\text{RuCl}_3$  (5 mg/ml), and  $^{103}\text{Ru}$ . Heat for 10 min to allow isotope exchange to be completed. Acidify the solution to  $\text{pH} = 1$  with  $\text{H}_2\text{SO}_4$  to evaporate the  $\text{RuO}_4$ . Heat for 30 min.
8. Repeat step 7 two times.
9. Acidify solution to 1 N  $\text{H}_2\text{SO}_4$ . Add 1 ml 30%  $\text{H}_2\text{O}_2$ . Dilute to 70 ml.
10. Extract with 35 ml 5% tri-isooctylamine (TIOA)/xylene. Shake for 5 min. Discard the aqueous phase. Wash with 50 ml 1 N  $\text{H}_2\text{SO}_4$  containing a few drops 30%  $\text{H}_2\text{O}_2$ . Shake for 2 min.
11. Back extract with 20 ml 0.5 N  $\text{NaOH}$  two times. Shake for 2 min.
12. Evaporate solution to 20 ml for electrodeposition. The current is 300 mA. The time is about 5 h (or overnight). The results are shown in Table 4 (see Appendix 1).

**Flow sheet of the procedure for 200 litres sea water.**

1.

- 1) Filter 200 litres sea water through 4 filters (filter paper).  
This takes 1 h.
- 2) Add  $^{99m}\text{Tc}$  and 100 ml 30%  $\text{H}_2\text{O}_2$ . Stir to uniformity to get  $\text{TcO}_4^-$  and allow the isotope exchange to be completed. Let stay for 30 min.
- 3) Acidify the 200 litres sea water to  $\text{pH} = 1$  with conc.  $\text{H}_2\text{SO}_4$ . Stir with air pump for 1 h.



2.

- 1) Add anion ion exchange AG 1- $\text{X}_4$  resin (100-200 mesh) to the beaker with 1 N  $\text{H}_2\text{SO}_4$  and stir to uniformity.
- 2) Make a column which is 11 cm long and with a diameter of 2.5 cm in 1 N  $\text{H}_2\text{SO}_4$ .
- 3) Add the sea water to three parallel columns. The speed is about 50 ml/min for each column. This takes 22 h.
- 4) Wash each column with 500 ml ion exchange water, 500 ml 0.1 N  $\text{HNO}_3$  and 100 ml 1 N  $\text{HNO}_3$ .
- 5) Strip the Tc with 200 ml 10 N  $\text{HNO}_3$  for each column. Eluate with 25 ml for each column and wait for 80 min for the ion exchange. Use about 2 h for stripping.



3.

- 1) Add a few drops  $\text{AgNO}_3$  carrier. Evaporate the 600 ml stripping solution to 0.5 ml.
- 2) Add 0.5 ml 10 N  $\text{H}_2\text{SO}_4$ . Dilute to 20 ml. Add 1 ml 5%  $\text{NaClO}$ . Heat for 10 min.



4.

- 1) Dilute to 50 ml. Add 0.5 ml 20 mg/ml  $\text{AgNO}_3$  and 0.5 ml 10 mg/ml  $\text{FeCl}_3$ . Add  $\text{NaOH}$  to  $\text{pH} = 9$ . Heat for 5 min. Filter the solution. Wash the precipitate three times with water ( $\text{pH} = 9$ ). Discard the precipitate.





- ↓
- 5.
- 1) Add 0.5 ml 5 mg/ml  $\text{RuCl}_3$  and 1 ml 5%  $\text{NaClO}$ . Keep pH = 9. Heat for 10 min to allow the isotope exchange to be completed and to get  $\text{RuO}_4^-$ . (The solution should be bright yellow. If it is not add more 5%  $\text{NaClO}$ ). Add 1 ml 5%  $\text{NaClO}$ .
  - 2) Acidify the solution to pH = 1 with 10 N  $\text{H}_2\text{SO}_4$ .
  - 3) Heat for 15 min in order to evaporate the  $\text{RuO}_4$ . The bright yellow disappears and solution is colourless.

- ↓
- 6.
- 1) Transfer solution to another beaker. Keep the volume at 70 ml.
  - 2) Repeat step 5.

- ↓
- 7.
- 1) Transfer solution to another beaker. Keep the volume at 70 ml.
  - 2) Repeat step 5.

- ↓
- 8.
- 1) Acidify solution to 1 N  $\text{H}_2\text{SO}_4$ . Add 1 ml 30%  $\text{H}_2\text{O}_2$  and dilute to 100 ml.
  - 2) Extract with 80 ml 5% TIOA (tri-isooctylamine)/xylene. Shake for 5 min.
  - 3) Wash with 80 ml 1 N  $\text{H}_2\text{SO}_4$  containing 0.5 ml 30%  $\text{H}_2\text{O}_2$ . Shake for 2 min.
  - 4) Wash with 80 ml  $\text{H}_2\text{O}$ . Shake 5 min.

- ↓
- 9.
- 1) Backextract with 40 ml 0.5 N  $\text{NaOH}$ . Shake for 2 min.
  - 2) Backextract again with 20 ml 0.5 N  $\text{NaOH}$ . Shake for 2 min. Combine the two solutions.
- ↓



- 10.
- 1) Evaporate the solution to 20 ml for electrodeposition.
  - 2) The current is 300 mA. The time is at least 5 h or overnight (about 10-24 h).
  - 3) Wash the plate with pH = 9 water once.
  - 4) Count the chem. yield.

Flow sheet of the procedure collecting the  $^{99}\text{Tc}$  from  $\text{Fe}(\text{OH})_2$  (see Appendix 2).

Flow sheet of analysis of the seaweed (see Appendix 3).

# Results and Discussion

## Anion exchange

The  $\text{TcO}_4^-$  is intensely absorbed on anion exchange AG1-X<sub>4</sub> (100-200 mesh) in 0.1 N -1 N  $\text{H}_2\text{SO}_4$ . Technetium-99 is efficiently collected with 3 columns (11 × 2.5 cm AG 1-X<sub>4</sub>) from 200 litres (6 columns for 400 litres and 1 for 50 litres of sea water). Technetium-99 is concentrated from a large amount of salt. The columns are washed with ion exchange water, 0.1 N  $\text{HNO}_3$ , and 1 N  $\text{HNO}_3$ , for decontaminating from one, two and three valence cation nuclides. Technetium is successfully stripped with 200 ml 10 N  $\text{HNO}_3$  for each column. It takes 2 h for stripping  $^{99}\text{Tc}$ . The  $\text{HNO}_3$  is easily evaporated for next step purification. The chemical yield of  $^{99}\text{Tc}$  for anion exchange is about 95%. Technetium loss in the column is about 5%. The sea water must be filtered because the organic matter and dirt will destroy the column and thus decrease the chemical yield of technetium.

There are three alternative methods shown in Table 1 for anion exchange of 200 litre sea water:

- a) The technetium is oxidized by  $\text{H}_2\text{O}_2$  in 0.1 N  $\text{H}_2\text{SO}_4$
- b) The technetium is oxidized by oxygen in air (from air pump)
- c) The technetium-99m is reduced to  $^{99\text{m}}\text{Tc}^{+4}$  with  $\text{K}_2\text{S}_2\text{O}_5$ .

Then the  $^{99\text{m}}\text{Tc}^{+4}$  is added to 200 litre of sea water. Stir with air pump for 1 h. Technetium could be oxidized by oxygen in air (from air pump). By the 3 methods, the same chemical yields of  $^{99\text{m}}\text{Tc}$  are obtained. It is shown that the  $\text{Tc}^{+4}$  could not be stable in solution without a reducing agent. The  $\text{Tc}^{+4}$  could easily be oxidized by a gentle oxidizing agent such as  $\text{H}_2\text{O}_2$  and  $\text{O}_2$ . So the technetium valence state in the sea water will be  $\text{TcO}_4^-$ , because the sea water contains oxygen.

## Ruthenium decontamination

Technetium and ruthenium are oxidized to  $\text{TcO}_4^-$  and  $\text{RuO}_4^-$  by  $\text{NaClO}$  at pH = 9. Acidify the solution to pH = 1 with  $\text{H}_2\text{SO}_4$ . In this case, the  $\text{RuO}_4$  is evaporated at 100°C in 0.1N  $\text{H}_2\text{SO}_4$ . But the  $\text{TcO}_4^-$  is left in solution, as shown in Tables 2 and 3. This step is very efficient and convenient for ruthenium decontamination instead of  $\text{CCl}_4$  extraction, but the evaporation (and extraction of  $\text{CCl}_4$ ) of the  $\text{RuO}_4$  are interferred with by organic agents and iron. If the solution does not change to a bright yellow colour, it is necessary to add more  $\text{NaClO}$ . The solution may be evaporated to near dryness to remove organic agents, or  $\text{Fe}(\text{OH})_3$  may be precipitated in order to remove the iron.

Technetium and ruthenium are separated by extraction of TIOA/xylene at controlled valence with  $\text{H}_2\text{O}_2$ . If the solution contains concentrated  $\text{Na}_2\text{SO}_4$ , the extraction rate of technetium is decreased. The different valence states of ruthenium are controlled with  $\text{NaClO}$  and  $\text{H}_2\text{O}_2$  in different steps in the procedure to get higher ruthenium decontamination. The decontamination factors of ruthenium for each step in the procedure are shown as follows:

Step	Decontamination factors of Ru
Anion exchange	5
Evaporation in 0.1 N H <sub>2</sub> SO <sub>4</sub>	$2 \times 10^7$
5% TIOA/xylene extraction	250

According to the step-by-step decontamination of the procedure, the decontamination factor for ruthenium should be  $2.6 \times 10^{10}$ . But the large volume of sea water is more complicated, as it contains many interfering elements. Furthermore, the low count of  $^{103}\text{Ru}$  used for the decontamination test may present problems. So the decontamination of the procedure is only  $2.5 \times 10^5$ - $2.4 \times 10^7$  for ruthenium,  $1.66 \times 10^5$  for  $^{110\text{m}}\text{Ag}$ . Technetium is lost at each step of the procedure as follows:

Step	Loss rate of $^{99\text{m}}\text{Tc}$ %
Left on column	$\sim 5$
Fe(OH) <sup>3</sup> scavenging and AgCl precipitate	$\sim 10$
evaporation operation	$\sim 5$
5% TIOA/xylene extraction	$\sim 5$
Electrodeposition	$\sim 5$

The chemical yield of the procedure is about 70%.

## Conclusion

1.  $\text{TcO}_4^-$  is intensely absorbed on anion exchange AG1-X<sub>4</sub> resin in 0.1 N-1 N  $\text{H}_2\text{SO}_4$ .  $\text{TcO}_4^-$  is stripped with 10 N  $\text{HNO}_3$ . Use 2 hours for the stripping. The chemical yield of technetium is about 95%.
2. Three columns (11 × 2.5 cm of AG 1-X<sub>4</sub> 100-200 mesh) anion exchange are efficiently used for collecting technetium in a 200-litre sea water sample.
3. Ruthenium and technetium are oxidized to  $\text{RuO}_4^-$  and  $\text{TcO}_4^-$  with  $\text{NaClO}$  at pH = 9. Acidify to 0.1 N  $\text{H}_2\text{SO}_4$ . Heat for 10 min at 100°C. 99.64% of  $\text{RuO}_4$  is evaporated and the  $\text{TcO}_4^-$  is left in solution. Repeat the operation 3 times; the decontamination for ruthenium is  $2 \times 10^7$ . It is more convenient and efficient compared with  $\text{CCl}_4$  extraction.
4.  $\text{Fe(OH)}_3$  scavenging, extraction of 5% TIOA/xylene are used for ruthenium decontamination and other nuclides. AgCl precipitate is used for  $^{110\text{m}}\text{Ag}$  decontamination.
5. The procedure can be applied to different types of environmental samples. The average chemical yield for Tc is about 70%, and the decontamination factors are  $2.5 \times 10^5$ - $2.4 \times 10^7$  for ruthenium and  $1.66 \times 10^5$  for  $^{110\text{m}}\text{Ag}$ . The reproducibility of the method is satisfactory ( $\pm 10\%$ ).

## References

1. S. Foti et al. Anal. Chem. Acta 60, 269 (1972).
2. Q.J. Chen et al. Risø-M-2671.
3. E. Anders, NAS-NS-3021.

Table 1. Chemical yield of  $^{99m}\text{Tc}$  for anion exchange at different conditions of 200 litres sea water and  $^{99}\text{Tc}$  Bq/m<sup>3</sup> (Klint sea water March 1988 in Denmark)

Condition	$^{99m}\text{Tc}$ valence state	No.	Sea water volume litre	Columns number 11 × 2.5 cm	Stripping volume 10 N HNO <sub>3</sub> ml	Time for stripping min	$^{99m}\text{Tc}$ counts before exchange c.p.m.	$^{99m}\text{Tc}$ counts after exchange c.p.m.	Chemical yield %	$^{99}\text{Tc}$ Bq/m <sup>3</sup>	(Mean ± 1 SD %) $^{99}\text{Tc}$ Bq/m <sup>3</sup>
Filter	$\text{TcO}_4^-$	1	200	3	450	90	28118	25083	89.2	-	
0.1 N H <sub>2</sub> SO <sub>4</sub>		2	200	3	600	120	40594	37875	93.3	0.4427	
0.5 ml H <sub>2</sub> O <sub>2</sub>		3	400	4	800	120	25176	20929	83.3	0.4862	
per litre Pump air		4	200	3	600	120	8640	7736	89.5	0.5230	
Filter	$\text{TcO}_4^-$	1	200	3	600	120	30798	28946	94.0	0.4961	0.4841 ± 0.0450 (± 9.3%)
Pump air		2	200	3	600	120	314755	303757	96.5	0.4116	
Filter	$\text{Tc}^{+4}$	1	200	3	600	120	48502	46348	95.6	0.4861	
Pump air $^{99m}\text{Tc}^{+4}$		2	200	3	600	120	48444	46022	95.0	0.5432	

**Table 2. Determination of evaporation rate of  $\text{RuO}_4$  in 0.1 N  $\text{H}_2\text{SO}_4$  at 100°C**

No.	Evaporation time min	Before evaporation counts c.p.s.	After evaporation counts c.p.s.	Loss chemical yield of $^{103}\text{Ru}$ %	Decontamination factor
1	5	276.84	3.63	98.59	76
2	5	267.29	3.26	98.78	82
1	10	373.71	1.33	99.64	281
2	10	266.35	0.99	99.63	269

**Table 3. Determination of evaporation rate of  $^{99\text{m}}\text{Tc}$  in 0.1 N  $\text{H}_2\text{SO}_4$  at 100°C**

No.	Ruthenium carrier 5 mg/ml $\text{RuCl}_3$	Evaporation time min	Before evaporation counts c.p.s.	After evaporation counts c.p.s.	Chemical yield %
1	0.1 ml	90	2450	2493	101.8
2	0.1 ml	90	2450	2568	104.8
1	0.4 ml	90	2450	2592	105.8
2	0.4 ml	90	2450	2524	103.0
1	0.8 ml	90	2450	2524	103.0
2	0.8 ml	90	2450	2494	101.8

**Table 4. Chemical yield of technetium and decontamination factor of  $^{103}\text{Ru}$  of the procedure**

No.	Nuclides	Before the procedure counts c.p.s.	After the procedure counts c.p.s.	$^{99\text{m}}\text{Tc}$ chemical yield %	$^{103}\text{Ru}$ decontamination factor
1	$^{99\text{m}}\text{Tc}$	78.61	62.63	79.7	
2	$^{99\text{m}}\text{Tc}$	45.58	36.33	79.3	
3	$^{99\text{m}}\text{Tc}$	22.08	14.37	65.1	
1	$^{103}\text{Ru}$	448.73	0.00180		$2.5 \times 10^5$
2	$^{103}\text{Ru}$	400.04	0.00125		$3.2 \times 10^5$
3	$^{103}\text{Ru}$	665.0	0.0000272		$2.4 \times 10^7$

## Appendix 2

### Determination of $^{99}\text{Tc}$ in environmental samples by anion ion exchange (Collecting $^{99}\text{Tc}$ by $\text{Fe}(\text{OH})_2$ )

Sample: Containing  $^{99}\text{Tc}$ , 32 grams  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 5-10 litres sea water. (Collect the sample by  $\text{Fe}(\text{OH})_2$ ).

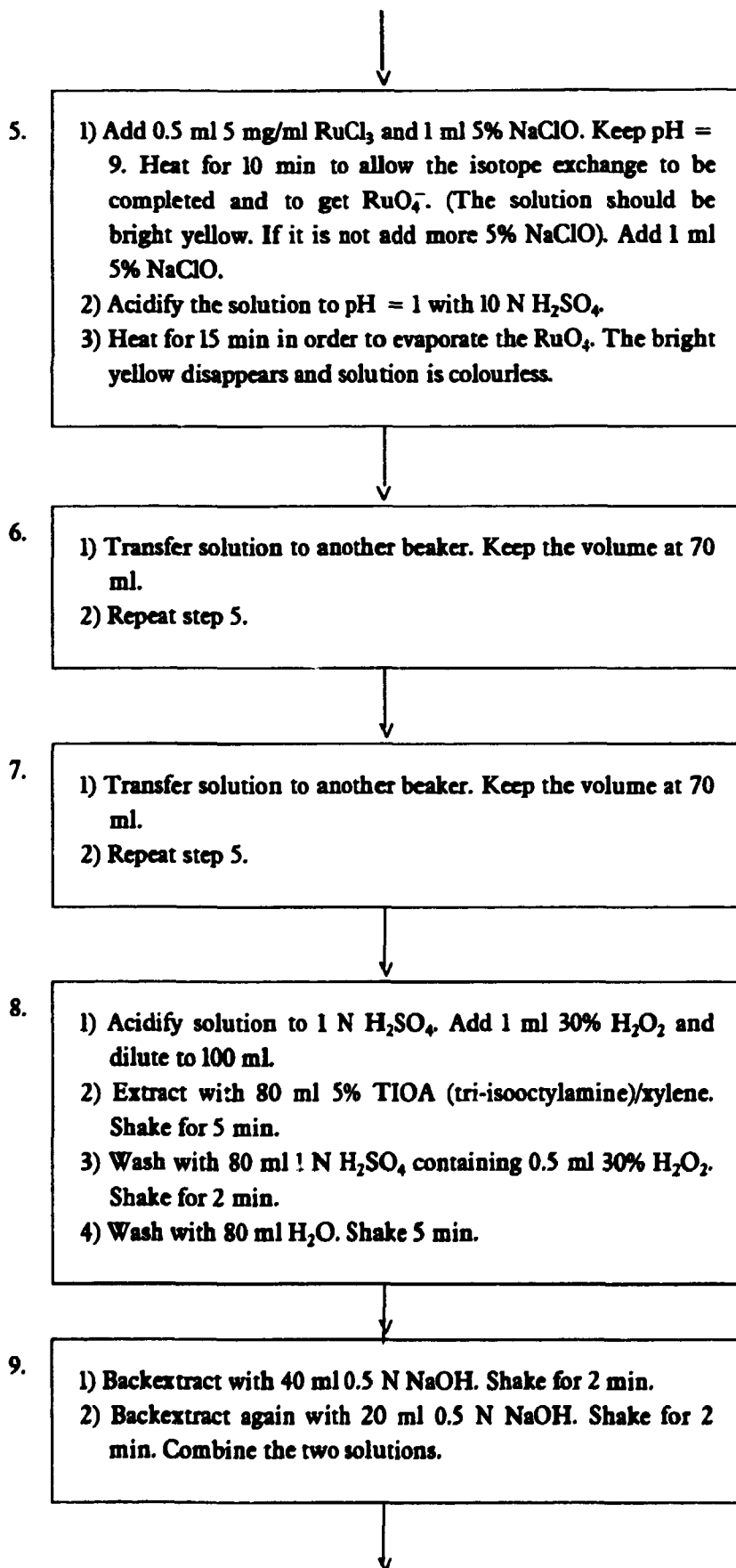
1.
  - 1) Acidify the sample solution to 0.3-0.5 N  $\text{H}_2\text{SO}_4$ . Let stay for a few days in order to dissolve.
  - 2) Add  $^{99}\text{mTc}$  and 15 ml 15%  $\text{NaClO}$ . Shake until uniform to allow the isotope exchange to be completed. Stand for 1 h.
  - 3) Filter the solution.

2.
  - 1) Add anion ion exchange AG 1- $\text{X}_4$  resin (100-200 mesh) to beaker with 1 N  $\text{H}_2\text{SO}_4$  and stir to get a uniform mixture.
  - 2) Prepare a column: 11 cm  $\times$  2.5 cm in 1 N  $\text{H}_2\text{SO}_4$ .
  - 3) Add the solution to column. The flow rate is 30 ml/min.
  - 4) Wash with 300 ml ion exchange water, 300 ml 0.1 N  $\text{HNO}_3$  and 100 ml 1 N  $\text{HNO}_3$ .
  - 5) Strip the Tc with 200 ml 10 N  $\text{HNO}_3$ . First eluate with 25 ml and wait for 80 min for the ion exchange. It takes about 2 h for stripping.

3.
  - 1) Add a few drops  $\text{AgNO}_3$  carrier. Evaporate the 200 ml stripping solution to 0.5 ml.
  - 2) Add 0.5 ml 10 N  $\text{H}_2\text{SO}_4$ . Dilute to 20 ml. Add 1 ml 5%  $\text{NaClO}$ . Heat for 10 min.

4.
  - 1) Dilute to 70 ml. Add 0.5 ml 20 mg/ml  $\text{AgNO}_3$  and 0.5 ml 10 mg/ml  $\text{FeCl}_3$ . Add  $\text{NaOH}$  to  $\text{pH} = 9$ . Heat for 5 min. Filter the solution. Wash the precipitate three times with water ( $\text{pH} = 9$ ). Discard the precipitate.







- 10.
- 1) Evaporate the solution to 20 ml for electrodeposition.
  - 2) The current is 300 mA. The time is at least 5 h or overnight (about 10-24 h).
  - 3) Wash the plate with pH = 9 water once.
  - 4) Count the chem.yield.

## Appendix 3

### Determination of $^{99}\text{Tc}$ in seaweed by TIOA extraction Flow sheet

1.
  - 1) Add to 10 g (10-20 g) dry powdered seaweed, 0.5 ml 5 mg/ml  $\text{RuCl}_3$ , 0.5 ml 20 mg/ml  $\text{AgNO}_3$ ,  $^{99\text{m}}\text{Tc}$  and 20 ml concentrated  $\text{H}_2\text{SO}_4$  (36 N) in a flask (see figure 2). Stir until completely mixed. (Per 1 g seaweed/2 ml conc.  $\text{H}_2\text{SO}_4$ ).
  - 2) Let stay for 1 h. The seaweed is carbonated by conc.  $\text{H}_2\text{SO}_4$ .
  - 3) Add conc.  $\text{HNO}_3$  (15 N) drop by drop to the flask. Be careful, the reaction is very strong. Continuously add conc.  $\text{HNO}_3$  (per 1 g seaweed/6-8 ml 15 N  $\text{HNO}_3$ ) until the reaction is calm.
  - 4) Heat the solution (in the flask). The reaction is continued until the mixture turns black.
  - 5) Add conc.  $\text{HNO}_3$ . The black colour disappears. Continuously heat the solution and the black colour returns.
  - 6) Repeat step 5) until the solution becomes greenish yellow.



2.
  - 1) Transfer the solution to 300 ml beaker. Dilute to 200 ml (the acid concentration is 5-6 N).
  - 2) Add 10 g  $\text{K}_2\text{S}_2\text{O}_8$  and heat for 10 min.
  - 3) Cool and filter the solution.



3.
  - 1) Transfer the solution to 500 ml separator.
  - 2) Extract with 80 ml 5% TIOA (tri-isooctylamine)/xylene. Shake for 2 min.
  - 3) Wash with 80 ml 1 N  $\text{H}_2\text{SO}_4$  containing 0.5 ml 30%  $\text{H}_2\text{O}_2$ . Shake for 2 min.
  - 4) Wash with 80 ml  $\text{H}_2\text{O}$ . Shake 5 min.
  - 5) Backextract with 40 ml 0.5 N  $\text{NaOH}$ . Shake for 2 min.
  - 6) Backextract again with 20 ml 0.5 N  $\text{NaOH}$ . Shake for 2 min. Combine the two solutions.



4.
  - 1) Evaporate the solution to 20 ml for electrodeposition.
  - 2) The current is 300 mA. The time is at least 5 h or overnight (10-24 h). The chemical yield is 50-75%.

*Figure 1.*

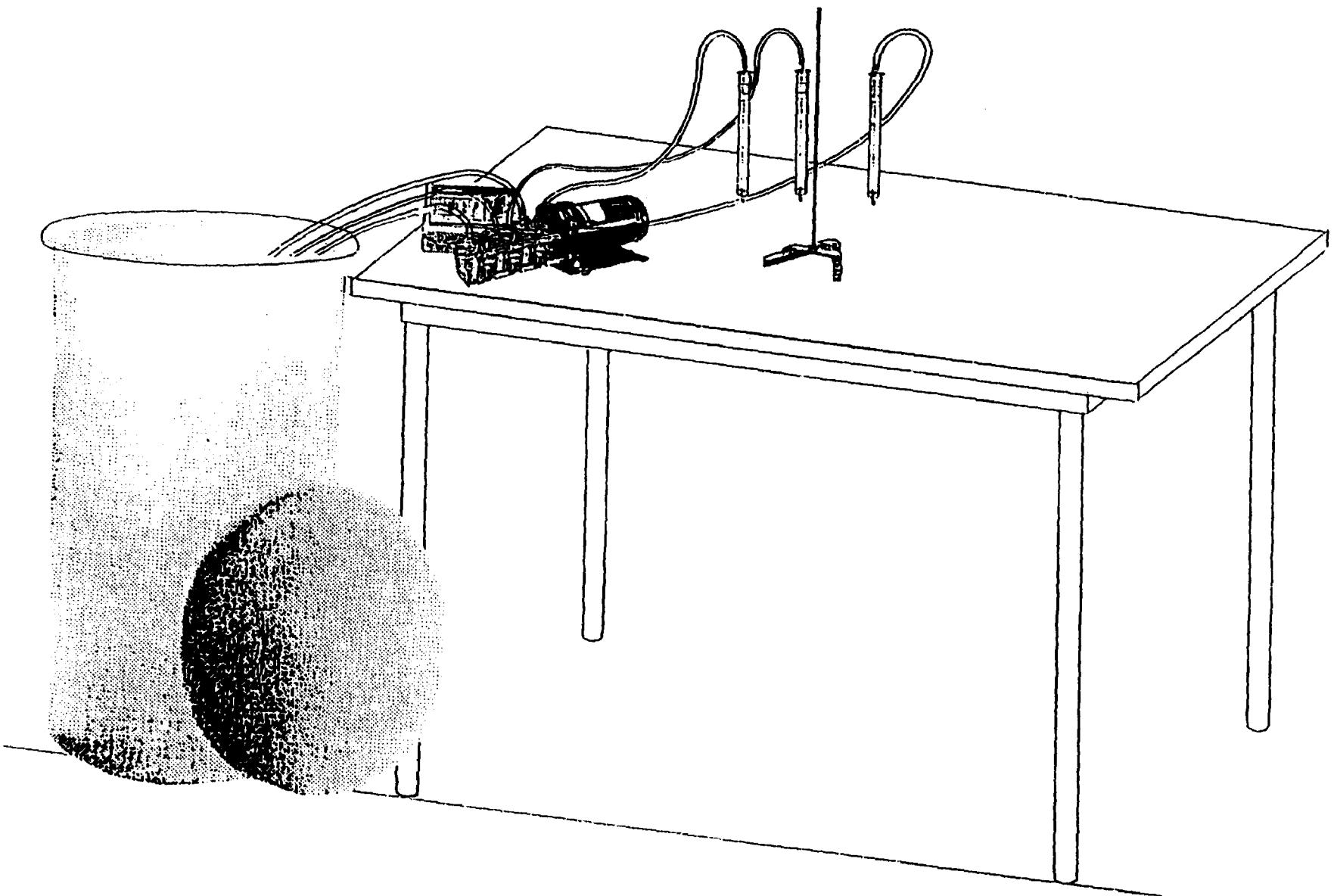
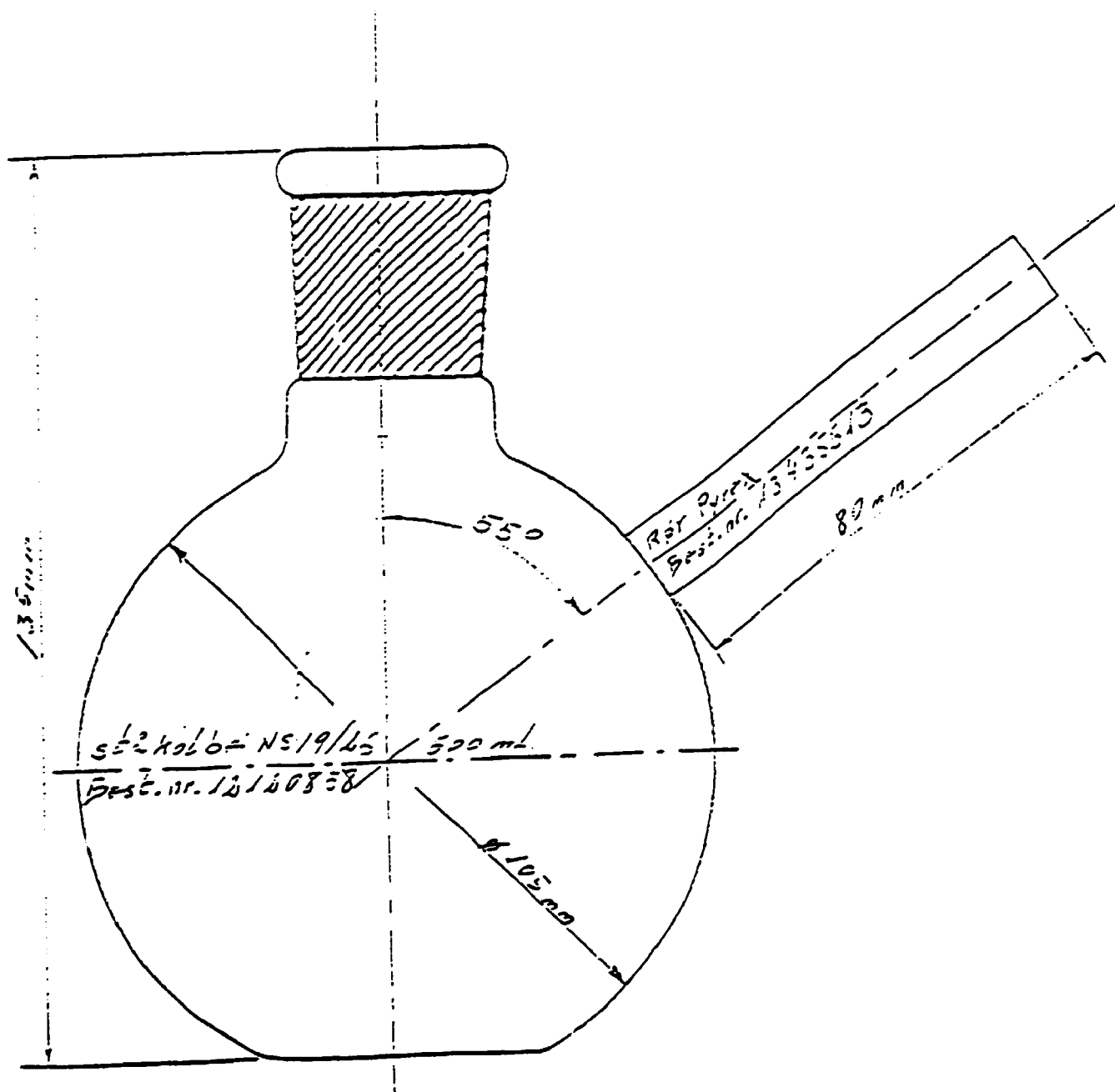


Figure 2



# Bibliographic Data Sheet

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Risø National Laboratory

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**Abstract (Max. 2000 char.)**

The chemical yield of technetium by an anion exchange (AG 1-X<sub>4</sub>) procedure is determined under different conditions from 200 liters sea water. A new method for collecting  $^{99}\text{Tc}$  from 200-400 liters sea water has been developed by anion exchange. The evaporation rates of  $\text{RuO}_4$  and  $\text{TcO}_4^-$  are determined at  $100^\circ\text{C}$  in 0.1 N  $\text{H}_2\text{SO}_4$ . A higher decontamination factor  $2.5 \times 10^5 - 2.4 \times 10^7$  for ruthenium is obtained by evaporating the  $\text{RuO}_4$  at  $100^\circ\text{C}$  in 0.1 N  $\text{H}_2\text{SO}_4$ . The ruthenium is oxidized to  $\text{RuO}_4^-$  with  $\text{NaClO}$  at  $\text{pH} = 9$ .  $\text{Fe}(\text{OH})_3$  scavenging,  $\text{AgCl}$  precipitation and 5% TIOA/xylene extraction at controlled valence are used for decontamination of ruthenium,  $^{110\text{m}}\text{Ag}$  and other nuclides. The chemical yield of technetium-99 in the procedure is about 70%.

**Descriptors - INIS/EDB**

EFFICIENCY; EVAPORATION; EXCHANGE; ION; PH VALUE; QUANTITATIVE CHEMICAL ANALYSIS; RUTHENIUM 103; SEAWATER; SEAWEEDS; SILVER 110; SOLVENT EXTRACTION; TECHNETIUM 99

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